DEPARTMENT OF ECOLOGY

MEMORANDUM

TO: Interested Persons

FROM: Steve Robb

DATE: August 28, 1997

SUBJECT: Total Petroleum Hydrocarbons

This memo is intended to provide a summary of the current work underway by the Duwamish Coalition Brownfields TPH Project to develop petroleum hydrocarbon cleanup levels for the Model Toxics Control Act (MTCA).

At this time, draft rule language is not being proposed because there are too many inter-dependent issues. It is felt it is premature to draft rule language that could be mis-leading and confusing without more context for the draft language, context that is not complete. However, certain issues have been developed and are included in this memo as to what *could* be part of draft rule language.

If there are questions regarding this memorandum, you can contact me (after September 10) at 360-407-7188 or by e-mail at srob461@ecy.wa.gov.

SUMMARY

This is provided by Ecology for informational purposes only and does not necessarily represent decisions of the Duwamish Coalition TPH Brownfields Project Oversight Group (POG) or Ecology. All issues are still subject to change. The terminology is also subject to change.

Framework

The proposed framework for petroleum hydrocarbons ("total petroleum hydrocarbons"--TPH) employs two new concepts. The first concept is use of the fractionation/surrogate approach as an alternative to measuring the constituents of the petroleum mixture. The surrogate approach uses carbon fractions within the TPH mixture that are representative of the overall contaminant blend with respect to factors such as mobility, fate, and toxicity.

The second concept is to incorporate a tiered risk-based approach into MTCA Method B and C cleanup level scenarios. These tiers are modeled on the American Society for Testing and Materials (ASTM) Risk Based Corrective Action (RBCA) three-tiered evaluation process for assessing the risk of contaminants at a site, with higher tiers representing sites of increased complexity. The Ecology TPH framework will also include a lower level tier (a fourth tier) to allow cleanups under the traditional Method A approach (no fractionation necessary). The intent of the new framework is for sites to set cleanup levels as early in the evaluation as possible and only proceed to higher tiers when site complexity requires it. Cleanup levels in higher tiers are both site-specific and risk-based.

The Ecology TPH tiered process may be expanded so it not only evaluates human health risk but also environmental risk to plants and animals, both terrestrial and aquatic. However, many technical and policy issues need to be resolved prior to being available as rule, especially for aquatic.

Ecology's new TPH framework will include necessary changes to reflect the state's legal requirements and Ecology's policy decisions. A TPH guidance will be prepared to assist the user.

Summary of the TPH Tiers

Tier 0 (or Method A) is an easy to use tier that provides cleanup levels for TPH fuel types (not using a fractionation approach) and individual TPH chemicals of concern, such as benzene. This tier is designed to be protective of any type of land use. Therefore, the cleanup level is lower than other tiers. A site assessment to support Tier 0 should include non-fractionated TPH data, indicator chemical data, and chemical concentrations that are likely to represent the most impacted areas at the site.

Tier 1 is slightly more complex than Tier 0 , but still easy to use. The main difference from Tier 0 is a general consideration of exposure pathways and use of fractionated TPH data in Tier 1. Information on exposure pathways should be obtained through the development of a Conceptual Site Model (CSM).

Tier 2 is a site-specific assessment. Tier 2 requires obtaining exposure and/or fate and transport information that are more specific to the site, in addition to fractionated TPH data. The CSM will guide the information needs.

Tier 3 is the most complex site assessment and could be compared to a traditional baseline risk assessment. Ecology expects that very few sites will progress as far as Tier 3.

Any Tier 1, 2, or 3 site assessment should provide, at a minimum, the following data:

- Determination of actual or potential exposure pathways;
- Identification of chemical source area(s) and maximum concentrations of chemicals of concern;
- Identification of site conditions which affect or limit chemicals of concern; and
- Proof of no ongoing NAPL (non-aqueous phase liquids) release to groundwater.

TPH Chemistry

An important way this TPH tiered framework can be "risk-based" is by knowing the chemistry of the petroleum hydrocarbons *at the site* and how the physical, chemical, and toxicological properties of those hydrocarbons will relate to those factors that drive human health and/or ecological protection: exposure to the contaminants, toxicity of the contaminants, and how the contaminants may move and change.

Because petroleum hydrocarbons are mixtures of many substances, most of which we do not have the necessary data for, the fraction/surrogate approach will be used. In this approach, those individual substances we can identify and have data for such as the "BTEX" (benzene, toluene, ethylbenzene, and xylenes) are measured but in addition the rest of the hydrocarbons are quantified by smaller groupings, or fractions. Two divisions that can be made are by sorting the hydrocarbons as either "aliphatic" or "aromatic." These can be further sub-divided by the size of the molecules. It is recommended that for human health these be defined as follows:

Aliphatic hydrocarbons: Compounds consisting of carbon and hydrogen, derived principally from petroleum, coal, coal tars, and plant sources which are characterized by straight or branched chain arrangement of the carbon atoms. Composed of three subgroups: alkanes, alkenes, and alkynes.

(Note: In these definitions, "plant sources" does not mean plant materials ('biogenics") are included with TPH. The TPH definition should make this clear.)

Aromatic hydrocarbons: Compounds consisting of carbon and hydrogen, derived principally from petroleum, coal, coal tars, and plant sources which are characterized by one or more unsaturated cyclic rings typified by benzene.

Low Aliphatics: Aliphatic hydrocarbons with 6, 7, or 8 carbon atoms (Note: for gasoline contaminated sites the n-hexane is measured and the oral cleanup level for it set individually).

Middle Aliphatics: Aliphatic hydrocarbons with more than 8 carbon atoms but no more than 18 carbon atoms for the oral route and no more than 16 carbon atoms for the inhalation route.

High Aliphatics: Aliphatic hydrocarbons with more than 18 carbon atoms but no more than 36 carbon atoms for the oral route; no inhalation route.

Aromatics: Aromatic hydrocarbons with more than 8 carbon atoms (cleanup levels for aromatic hydrocarbons with less than 8 are set individually) and no more than 36 carbon atoms, plus benzene for the oral route; and no more than 16 carbon atoms, plus benzene, for the inhalation route. (Note: Benzene, an indicator chemical, only has a cleanup level determined by a cancer slope factor; therefore the concentration of benzene is added to the other aromatics for inclusion as a non-carcinogen.)

Human Health Risk Assessment Procedures

In MTCA, human health risk is primarily determined by the use of a standardized risk assessment using default values. What makes one contaminant different from another is primarily the

toxicological data. MTCA uses "reference doses" for non-carcinogens and "cancer potency (or "slope") factors" for carcinogens.

For those individual substances that toxicity data already is available for, nothing new will occur in how they are calculated. However, for some substances and the TPH fractions, "surrogates" will need to act as the toxicological data for the calculations. (Only non-carcinogen surrogates are used as there is no compelling evidence that the fractions should have carcinogen surrogates.)

The following reference doses (and reference concentrations for vapors that could be inhaled) are recommended: (Note: Only those that will not be available in IRIS or HEAST will be added to the rule, the others will be "look-up" as they currently are. Those not currently available are marked with an asterisk.)

Reference Doses

	Oral RfD (mg/kg-day)	Inhal. RfD
Chemicals		
Toluene	0.2	0.114
Ethylbenzene	0.1	0.286
Xylenes (total)	2	0.2
n-Hexane	0.06	
Naphthalene	0.04	0.00011
1,2-Dibromoethane*	0.00005	----
MTBE*	0.005	0.86
TPH Fractions		
Low Aliphatics*	2	0.06
Middle Aliphatics*	0.6	0.6
High Aliphatics*	2	----
Aromatics*	0.03	0.114

*Not available in IRIS or HEAST

What sort of levels will these numbers lead to as cleanup levels? For example, if calculations are made for *only* the ingestion pathway then Method B "residential soil" non-carcinogen cleanup levels are:

Chemicals	MTCA Method B (soils)
Toluene	16,000 ppm
Ethylbenzene	8,000 ppm
Xylenes (total)	160,000 ppm
n-Hexane	4,800 ppm
Naphthalene	3,200 ppm
1,2-Dibromoethane	4 ppm
MTBE	400 ppm

TPH Fractions

Low Aliphatics	160,000 ppm
Middle Aliphatics	48,000 ppm
High Aliphatics	160,000 ppm
Aromatics	2,400 ppm

Except for a very fresh spill, the last two chemicals (1,2 -dibromoethane and MTBE) will most likely only be found in groundwater (if at all) since they are so mobile. For groundwater, the Method B cleanup level for 1,2 dibromoethane would be 0.4 ppb and for MTBE it would be 40 ppb, for oral ingestion.

Each of these soil concentrations represent MTCA Method B soil calculations for "single substances" (hazard quotients at the maximum of 1). A mixture would calculate proportional to the chemicals and fractions in the mixture. These soil concentration do not account for other potentially existing exposure pathways such as the soil-to-groundwater pathway, ecological pathway, inhalation pathway, or others which may lower the levels shown above.

For carcinogens:

Oral Cancer Slope Factors (CSF) and Inhalation CSF

Chemical	CSF (kg)(day)/mg	Inhal. CSF (kg)(day)/mg
Benzene	0.029	0.029
Benzo(a)anthracene*	TEF	TEF
Benzo(a)pyrene*	7.3	6.1
Benzo(b)fluroanthene*	TEF	TEF
Benzo(k)fluoranthene*	TEF	TEF
Chrysene*	TEF	TEF
Dibenzo(a,h)anthracene*	TEF	TEF
Indeno (1,2,3-c,d) pyrene*	TEF	TEF
1,2-Dibromoethane	85	0.77
1,2-Dichlorethane**	0.091	0.091

**Not available in IRIS or HEAST

(In MTCA the Cancer Slope Factor is called the Cancer Potency Factor.)

The seven (per WAC 173-340-200) carcinogen polynuclear aromatic hydrocarbons (cPAHs) are marked with an asterisk (*). Currently in MTCA, they are calculated as benzo(a)pyrene (BAP). It is planned that "toxicity equivalent factors" (TEFs) will be used for the other six cPAHs. Thus, they would be set relative to BAP. What these factors are, exactly, is still being determined.

Under Current Development

There are many activities under current development:

- Analytical methodology;
- Vapor and leaching pathway fate and transport model approach;
- Recommendations for surrogate toxicity issue and for development of cleanup levels associated with the vapor (acute and chronic) and leaching pathways;
- Ecological guidance (TPH) for terrestrial and aquatic receptors;
- Case studies; and
- Continue development of TPH guidance document.

Analytical:

An analytical workgroup composed of volunteers from about 10 laboratories working to update the petroleum analytical methods Ecology published earlier this year. This will provide for improved analytical techniques, identify ways that performance can be better measured and validated, and tailor the techniques to the requirements necessary for all the pathways.

Fate and Transport:

Methods for deriving risk-based cleanup levels at each tier will address the potential for TPH migration through various environmental pathways, including volatilization, leaching and groundwater migration. Contaminant fate and transport models and screening tools (similar to those contained in EPA Soil Screening Guidance; as well as more complex models such as SESOIL, MOFAT, GWSCREEN, the Farmer model, Thibodeaux-Hwang model, and the Johnson & Ettinger models) are being evaluated to back-calculate "look-up" cleanup levels for TPH mixtures, fractions, and indicator compounds in Tier 0/1. Default values for site-specific and other model parameters have been reviewed and are proposed for the Tier 0/1 derivations. For Tier 2, the user can use the same limited set of models or tools to re-evaluate cleanup or remediation levels based on site-specific data. Tier 3 fate and transport analyses will be reserved for those sites with unusual complexity or where unique migration pathways may exist.

Analyses to date have shown some modeling results for specific contaminants to be very low; the protective soil cleanup levels for vapor migration may be below analytical detection limits. Alternate protocols for direct soil vapor and soil leach screening or are being considered. This approach will be examined further during the case studies.

Ecological Risk:

The TPH ecological scope of work (this work is in progress and major parts have only recently been initiated so it is clearest to identify what the scope of this work is) is to provide procedures to determine cleanup levels for soil and groundwater where ecological receptors are present and have

the potential to be adversely affected by petroleum hydrocarbon contamination. The scope of work for the contractor and Ecology consists of five subtasks:

- Terrestrial ecological risk assessment;
- Aquatic ecological risk assessment;
- Ecological risk assessment chapter for the TPH guidance;
- Technical policy support; and
- Technical management.

The TPH terrestrial risk assessment tasks include: Development of a tiered approach; identification of toxicity criteria; selection of exposure scenarios; a calculation of terrestrial risk-based screening levels; and identification of "toolbox methods" to measure exposure and effects in higher tiers.

The TPH aquatic ecological risk assessment is to provide a means to determine soil cleanup levels that will protect receptors in the aquatic environment (not "water quality"). Three approaches are being evaluated to determine if there is sufficient toxicity data that can be used to establish toxicity reference values (TRVs) for petroleum hydrocarbons in the aquatic environment. This includes the general model for non-chemical-specific narcosis; the Massachusetts Department of Environmental Protection's proposed surrogate chemicals; and product-specific toxicity tests such as being developed by the Consolidated Tenants Group at the San Francisco International Airport.

Since major components of this work are still in progress and only recently started, it is not clear what will be available to include in either proposed rule amendments or guidance. This is pioneering work and the need to be scientifically defensible is paramount. However, it is the intent of the participants to move forward at this time and complete as much as possible.

Case Studies:

Four case study sites have been selected to evaluate implementation of the draft TPH decision-making framework and guidance. The sites were selected to provide the broadest possible representation of TPH contaminants and potential or actual migration pathways including vapor release, leaching, and groundwater migration to surface water (to evaluate possible aquatic impacts). Results of the case studies will be used to: (1) evaluate and correct problems with framework/guidance implementation; (2) obtain additional information about successful approaches to evaluating fate and transport (especially the vapor pathway); and (3) develop an economic comparison (benefit analysis) of using the new framework over former approaches for evaluating TPH cleanup requirements.

Guidance:

The most significant product of the TPH project will be a guidance document that Ecology will (after assuring compliance with rules and policies) provide to those using the MTCA cleanup process for TPH. For your information on what such a guidance may contain, a list of the sections is provided (human health only at this time):

1. INTRODUCTION AND BACKGROUND

2. OVERVIEW OF THE TPH FRAMEWORK

3. CONCEPTUAL SITE MODEL

4. DATA COLLECTION AND EVALUATION

5. SCREENING A SITE: THE TIER 0/TIER 1 PROCESS

6. THE TIER 2 RISK ASSESSMENT PROCESS

7. THE TIER 3 RISK ASSESSMENT PROCESS

8. REFERENCES

APPENDIX A	TABLES WITH TIER 0 AND TIER 1 SCREENING LEVELS
APPENDIX B	TECHNICAL BACKGROUND FOR DEVELOPMENT OF TIER 0 AND TIER 1 HUMAN HEALTH SCREENING LEVELS
APPENDIX C	TECHNICAL BACKGROUND FOR DEVELOPMENT OF TIER 0 AND TIER 1 ECOLOGICAL SCREENING LEVELS
APPENDIX D	SUMMARY OF APPROACHES FOR ADDRESSING ACUTE RISKS AND NONAQUEOUS PHASE LEACHING TO GROUNDWATER
APPENDIX E	SUMMARY OF FATE AND TRANSPORT CONSIDERATIONS FOR THE TPH FRAMEWORK
APPENDIX F	RETROFITTING EXISTING TPH DATA
APPENDIX G	PRESUMPTIVE REMEDY GUIDANCE FOR TPH SITES

These are titles only, the sections are still under development; the titles may change or additions made.

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